# Hydrogenation of olefins by polymer-bound palladium(II) Schiff base catalyst

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## ABSTRACT

Chloromethylated poly(styrene-divinylbenzene) was modified into coordinating Schiff base bearing ligand which was subsequently complexed with palladium chloride and activated by using sodium borohydride. The polymer-supported palladium complex and activated catalyst were characterized by various techniques such as elemental analysis, X-ray photoelectron spectroscopy, atomic absorption spectroscopy, IR, far IR spectral studies, SEM and thermogravimetric analysis. Surface area measurements by BET method and swelling studies with different solvents for the catalyst were also carried out. Catalytic activity towards hydrogenation of 1-hexene, 1-heptene, 1-octene, cyclohexene, norbornadiene (nbd) and 1,5-cyclooctadiene (1,5-cod) was assessed. The influence of variation in temperature, pressure, concentration of the catalyst as well as the substrate and the nature of the solvent on the rate of the reaction was studied for a few olefins. Recycling ability of the catalyst was also evaluated.

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## 1. Introduction

Immobilization of active transition metal complexes on to a solid support has proved to be an attractive method for overcoming the inherent drawback of homogeneous catalyst: separation of the product and recovery of the catalyst after completion of the reaction [1–3]. Supports for catalytic systems can be inorganic or organic. Inorganic matrices have potential advantages of offering excellent chemical, thermal and mechanical stability. Highly dispersed inorganic materials with controlled particle dimension and pore diameter and dimension are commercially available. Some of the commonly used supports are molecular sieves, zeolites, clays, metal oxides, carbon, etc. [4].

The increasing familiarity with and confidence in the use of polymer resins in solid phase synthesis has invoked organic chemists to search for possibilities of employing polymers as catalyst supports and reagents [5].

Since the late 1960s, a range of polymeric supports have been utilized and reported. Among them hydrophobic polystyrene (PS)

resin beads crosslinked with divinylbenzene (DVB) are the most versatile solid support. Other crosslinking agents like ethylene glycol dimethacrylate (EGDMA) and tetraethyleneglycol diacrylate (TEGDA) have also been used [6–8]. The PS resins that are commonly used have particle size ranging from 90 to 200 μm [5]. PS beads are available with different functional groups such as chloromethylated, aminomethylated, carboxy, hydroxymethylated, etc. These functional groups can be easily derived from PS by simple organic transformation [6,9].

With all the different supports available commercially, PS is still the most popular polymeric material used in solid phase synthesis due to its inexpenseness, ready availability, mechanical robustness, chemical inertness and facile functionalization [10].

Heterogenized metal Schiff base complexes on solid supports have been used as catalysts for oxidation and epoxidation reactions [11–14]. Ayala et al. [15] have performed the hydrogenation of imines using a hybrid organic–inorganic catalyst obtained by immobilizing chiral salen palladium and nickel complex on mesoporous silica and zeolite as supports.

It is interesting to note that manganese Schiff base complex developed by Kochi and co-workers [16] was heterogenized by preparing a polymeric version [17]. Appropriate functionalized monomers with desired ligands were copolymerized with crosslinked monomers. The insoluble functionalized polymer matrix was complexed with Mn(III) ions. This polymer-bound transition metal complex was found to be active towards selective oxidation of olefins.

In this paper, we present the synthesis and characterization of polymer-bound palladium(II) Schiff base complex from Merrifield's
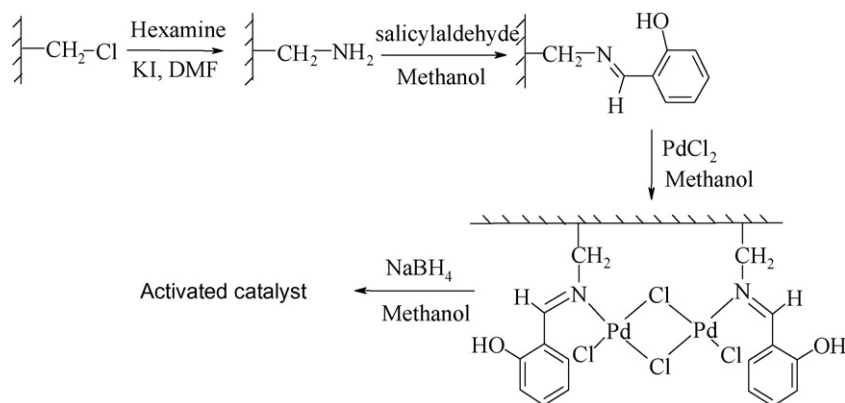
**Scheme 1.** Preparation of palladium Schiff base complex.

resin and its catalytic activity towards the hydrogenation of a few olefins.

## 2. Experimental

### 2.1. Materials and equipments

Chloromethylated poly(styrene-divinylbenzene) copolymer with 6.5% crosslinking (PSDVB) was obtained as a gift from Thermax India Ltd., Pune, India. Palladium chloride was obtained from Arora Matthey Ltd., India. Benzylamine, salicylaldehyde, 1,5-cyclooctadiene (1,5-cod), 1-hexene, 1-heptene, 1-octene, norbornadiene (nbd) and cyclohexene were purified and distilled before use. Super dry methanol was prepared according to a literature method. Hydrogen gas from cylinder was purified by passing it through saturated $KMnO_4$ solution, liquid paraffin, concentrated $H_2SO_4$ and solid KOH.

C, H and N analyses were carried out using a Thermo Finnegan Eager 300 analyzer at RRI, Bangalore and a Thermo Finnigan Flash EA1112 CHNS analyzer at Department of Organic Chemistry, I.I.Sc., Bangalore. Palladium was estimated by AAS using a GBC Avanta PM spectrophotometer and the IR spectra (in KBr) were recorded using a Shimadzu FTIR – 8400S spectrometer. Far IR spectra were recorded on an optical spectrometer Bruker IFS-66V/S. Surface area was measured using a Nova 1000 instrument in $N_2$ atmosphere. TGA studies were carried out using a Perkin-Elmer 7 series instrument. XPS was recorded at 35° take-off angle (relative to the surface normal) with an SSX-100 spectrometer using monochromatized Al Kα radiation (1486.6 eV). The analyzed core level lines were calibrated with respect to the component $C_{1S}$ of binding energy set at 285 eV. Scanning electron micrographs were recorded on a Leica S440i. GC was recorded on a Shimadzu gas chromatograph using a BP5 capillary column.

### 2.2. Preparation of (N-salicylidene benzylamine)PdCl$_2$ complex

7 ml of salicylaldehyde (5 mmol) was dissolved in minimum amount of ethanol and 5.3 ml of benzylamine (5 mmol) was added to it. The yellow solution obtained was refluxed on a hot water bath for 6 h. The mixture was then poured into ice cold water. N-salicylidene benzylamine (NSBA) was obtained as a yellow solid which was extracted with hexane and dried over anhydrous sodium sulphate and further purified by column chromatography.

The palladium Schiff base complex was prepared by refluxing a 1:1 mixture of N-salicylidene benzylamine (1 mmol) and $PdCl_2$ (1 mmol) in acetone (5 ml) for 10 h on a hot water bath. A brown crystalline complex of palladium separated out was filtered, washed with acetone and dried in vacuum.

### 2.3. Preparation of the polymer-bound palladium Schiff base complex

The chloromethylated polystyrene crosslinked with 6.5% divinylbenzene polymer beads (PSDVB) were first washed with a mixture of THF and $H_2O$ (4:1) using a Soxhlet extractor for 10 h and vacuum-dried. The PSDVB beads were modified into aminomethylated beads according to the literature method [18]. A mixture of 5 g of chloromethylated beads (6 mmol/g of Cl), 2 g of KI (12 mmol) and 1.68 g (12 mmol) of hexamine was suspended in 35 ml DMF and heated with stirring at 100 °C on an oil bath for 10 h. The suspension was poured into water and stirred for 30 min and filtered, and washed with 6N HCl and water. The beads were then stirred with 150 ml of 10% NaOH solution for 2 h, filtered, washed with methanol several times and allowed to swell for 1 h in methanol (50 ml). To this, 3 ml of salicylaldehyde was added and the mixture was refluxed on a water bath for 30 h. The beads were filtered, washed with methanol and dried. Later the beads were soaked in methanol for an hour and was refluxed with a solution of $PdCl_2$ (1.5 g ≈ 8.46 mmol Pd in 70 ml methanol) for about 12 h. The buff coloured beads were filtered, washed, Soxhlet-extracted with methanol and dried.

### 2.4. Catalyst activation

Supported palladium Schiff base complex was suspended in ethanol (25 ml) and $NaBH_4$ was added during which the supported complex changed from beige to grey. After 60 min the beads were filtered, washed with ethanol, dried and used for hydrogenation reactions.

### 2.5. Catalytic hydrogenation

The polymer-supported palladium complex was added to 30 ml of deaerated super dry methanol in the reaction system and allowed to be saturated in an atmosphere of $H_2$ for 1 h. The system was evacuated and again saturated with hydrogen gas. A known quantity of the olefin was injected into the system followed by releasing the system to a gas burette filled with hydrogen. The reaction was monitored by the volume of hydrogen absorbed at different intervals of time. The reaction mixture was injected into GC to confirm the product formation.

**Table 1**
Elemental analysis and physical properties of polymer and polymer-bound catalyst.

| | C% | H% | N% | Pd% | Pore diameter (Å) | Surface area (m²/g) | Apparent bulk density (g/ml) |
|---|---|---|---|---|---|---|---|
| Chloromethylated polystyrene divinyl benzene (PSDVB) | 74.47 | 6.25 | – | – | 84.79 | 35.45 | 0.42 |
| Amino methylated beads (PSDVBNH₂) | 80.57 | 7.13 | 4.26 | – | 81.21 | 40.10 | 0.43 |
| PS DVBNH₂-Salicylaldehyde (PSDVBNH₂-SAL) | 81.77 | 6.60 | 3.20 | – | 74.12 | 79.45 | 0.43 |
| PSDVBNH₂-SAL-PdCl₂ | 69.03 | 6.00 | 2.34 | 10.04 | 66.45 | 43.26 | 0.44 |
| PSDVBNH₂-SAL-PdCl₂-reduced with NaBH₄ (activated catalyst) | 64.86 | 5.78 | 2.33 | 9.20 | 61.80 | 35.85 | 0.46 |
| Recycled beads after 6 cycles | 67.00 | 5.90 | 4.98 | 9.20 | 64.95 | 35.10 | 0.45 |

## 3. Results and discussion

### 3.1. Characterization of the catalyst

Chloromethylated polystyrene (crosslinked with 6.5% divinylbenzene) beads were chemically modified into aminomethylated beads. These beads were then functionalized with salicylaldehyde to form Schiff base. The functionalized beads were then anchored with palladium chloride (Scheme 1). Elemental analysis results and physical properties of polymer and polymer-bound catalyst are given in Table 1.

Successful functionalization and loading of the metal was confirmed by various physicochemical analyses. Decrease in surface area of the beads on metal loading was observed, maybe due to blockage of pores of the polymer support after metal introduction. Similar observations have been reported for polymeric catalysts [19,20].

Scanning electron micrographs of polymer, functionalized beads and its complex were recorded to understand the morphological changes that occur at various stages. Smooth surface of the polymer beads is roughened on functionalization with benzimidazole and anchoring of metal. TGA studies of the activated catalyst show that it is stable up to a temperature of 200 °C (Fig. 1).

The ligand N-salicylidene benzylamine (NSBA) exhibits $\nu_{C=N}$ of azomethine group and $\nu_{OH}$ at 1631 and 3365 cm⁻¹ respectively [21]. The peak due to $\nu_{C=N}$ has shifted to 1614 cm⁻¹ on complexation. A broad peak in the complex at 3420 cm⁻¹ is assigned to $\nu_{OH}$ (Fig. 2). The far IR spectrum of the neat complex [PdCl₂(NSBA)] exhibits a peak at 358 cm⁻¹ assignable to $\nu_{Pd-O}$. In the neat complex, NSBA acts as a chelating bidentate ligand coordinating through N and O.

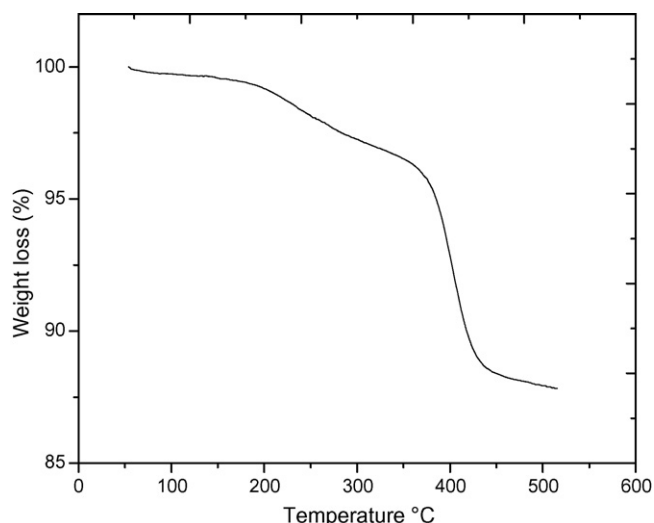Formation of Schiff base on the polymer support is indicated by a strong band at 1631 cm⁻¹ due to azomethine (C=N) stretching frequency [22] in the IR spectrum of the functionalized beads. This peak has undergone a shift from 1631 to 1637 cm⁻¹ after loading of palladium which suggests the coordination of nitrogen of the azomethine group to palladium [23] (Fig. 2). The $\nu_{OH}$ of the polymer-supported catalyst is found around 3400 cm⁻¹. The far IR spectrum of the heterogenized complex does not show any peak due to $\nu_{Pd-O}$ indicating that in the polymer-bound catalyst the oxygen of the phenolic–OH is not coordinated.

The X-ray photoelectron spectrum of palladium-anchored polymer beads exhibit peaks at 337.7 and 343.3 eV that are assigned to $3d_{5/2}$ and $3d_{3/2}$ of palladium(II), respectively (Fig. 3). On activation, the intensity of the peak is reduced, but the position of the peak at 338.6 eV still corresponds to $3d_{5/2}$ of palladium(II). The far IR spectrum of the palladium-anchored beads exhibits a broad intense band around 332 cm⁻¹ which may be assigned to both $\nu_{Pd-Cl_{terminal}}$ and $\nu_{Pd-Cl_{bridge}}$ [23] (Fig. 4). On activation with NaBH₄, this peak is shifted to 338 cm⁻¹ which is assigned to $\nu_{Pd-Cl_{terminal}}$. From XPS and far IR results, it is suggested that prior to activation, the metal is in a 2+ oxidation state and exists as a dimer, bridged by chloride ion.
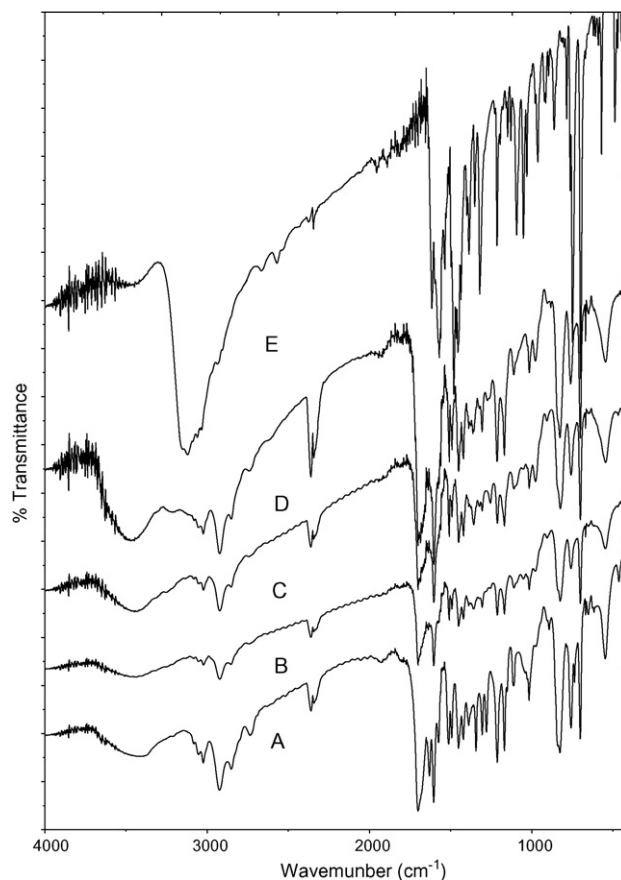


**Fig. 1.** TGA of the activated catalyst.



**Fig. 2.** Ir spectra of (A) PSDVBNH₂-SAL, (B) PSDVBNH₂-SAL-PdCl₂, (C) PSDVBNH₂-SAL-PdCl₂-reduced with NaBH₄, (D) recycled beads and (E) PdCl₂(N-salicylidene benzylamine) complex.
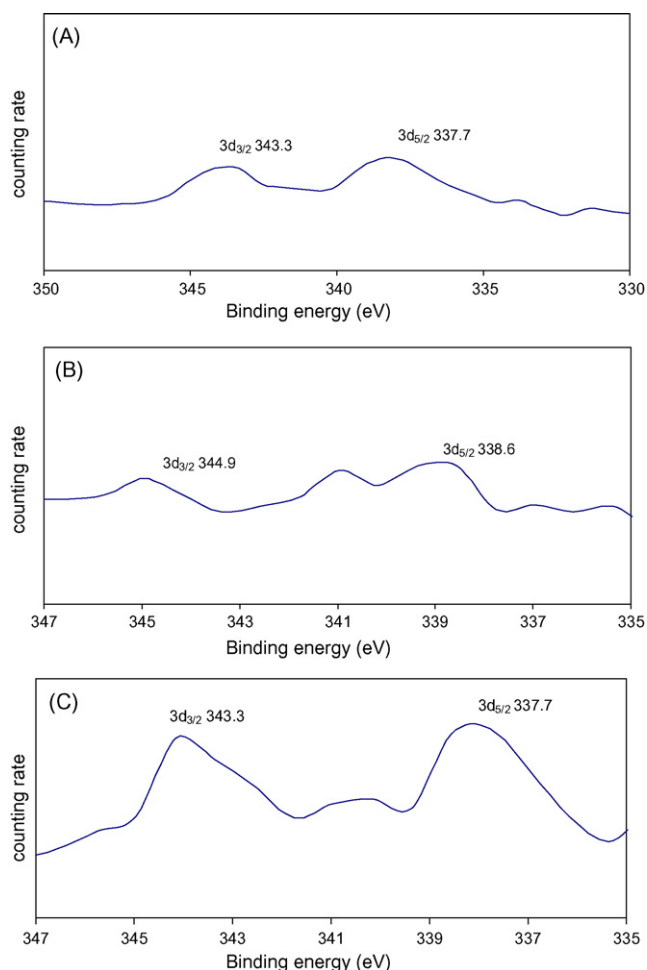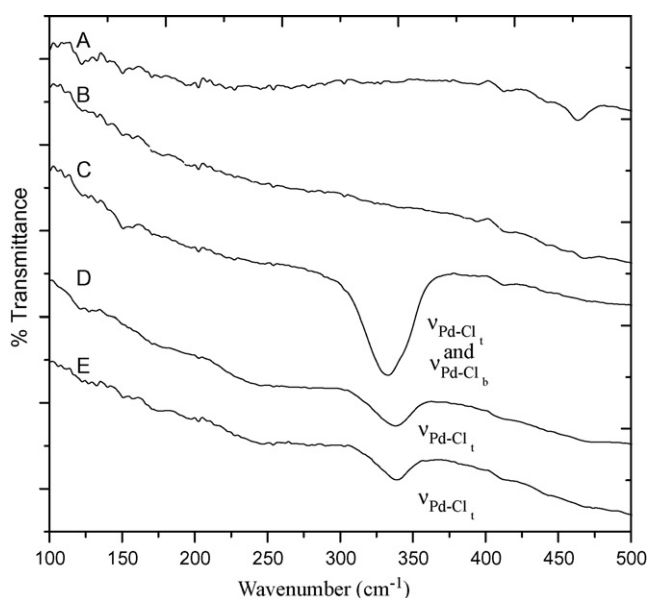
**Fig. 3.** XPS spectra of (A) PSDVBNH$_2$-SAL-PdCl$_2$, (B) PSDVBNH$_2$-SAL-PdCl$_2$-reduced with NaBH$_4$ and (C) recycled beads.



**Fig. 4.** Far IR spectra of (A) PSDVBNH$_2$, (B) PSDVBNH$_2$-SAL, (C) PSDVBNH$_2$-SAL-PdCl$_2$, (D) PSDVBNH$_2$-SAL-PdCl$_2$-reduced with NaBH$_4$ and (E) recycled beads.
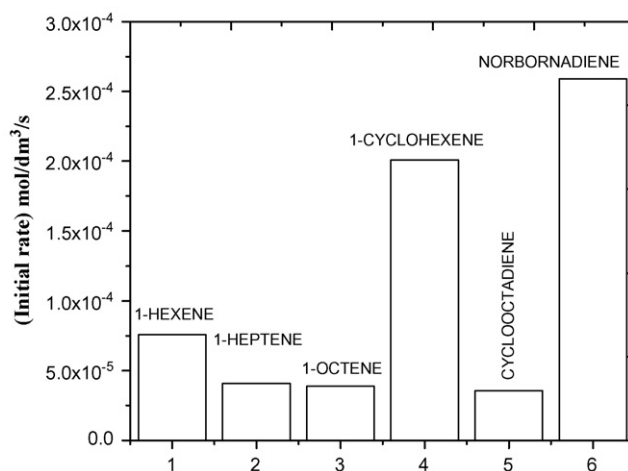


**Fig. 5.** Relative rate of hydrogenation of various substrates.

After activation with sodium borohydride, the metal still retains its 2+ oxidation state whereas the chloride bridge breaks resulting in mononuclear species. Similar observation has been made by Larson and Anderson [24] in their study on polymer-supported Cl$_2$Pd(pyridine)$_2$ complex. Reed et al. [25] and Collman et al. [26] have also reported the existence of such bridged species.

Swelling studies show that swelling increased with polar solvents than in nonpolar solvents. Methanol appears to be better suited for carrying out hydrogenation reactions since the miscibility of substrates and solubility of hydrogen is improved in methanol. Results of swelling studies are tabulated in Table 2.

### 3.2. Kinetics of hydrogenation

Preliminary reactions were carried out choosing 1-hexene, 1-heptene, 1-octene as terminal olefins, cyclohexene as cyclic olefin, 1,5-cyclooctadiene (1,5-cod) as cyclic diene and norbornadiene as bicyclic diene. The results of hydrogenation indicate that the reactivity order follows: norbornadiene > cyclohexene > 1-hexene > 1-heptene > 1-octene > 1,5-cyclooctadiene (Fig. 5). The order of reactivity may be explained based on steric and electronic factors. In case of terminal olefins, the decrease in activity from 1-hexene to 1-octene may be due to crowding in the transition state with increase in length of the carbon chain [8]. Usually the increase in carbon length enhances electronic transmission through inductive effect. But in this case, the steric effect dominates the reactivity rather than the electronic factor as the inductive effect is insignificant beyond the third carbon. Among the cyclic compounds, highly strained bicyclic norbornadiene undergoes rapid hydrogenation while the reactivity of 1,5-cod is minimal. It has been reported by several workers [27,28] that conjugated system such as 1,3-cod undergo hydrogenation faster compared to its nonconjugated isomer 1,5-cod which first undergoes isomerisation followed by hydrogenation.

**Table 2**
Swelling studies with different solvents.

| Solvent | Swelling (mole%) |
| --- | --- |
| Methanol | 1.85 |
| Ethanol | 1.37 |
| Acetonitrile | 1.20 |
| Acetone | 1.01 |
| THF | 0.97 |
| Benzene | 0.75 |
| Toluene | 0.58 |

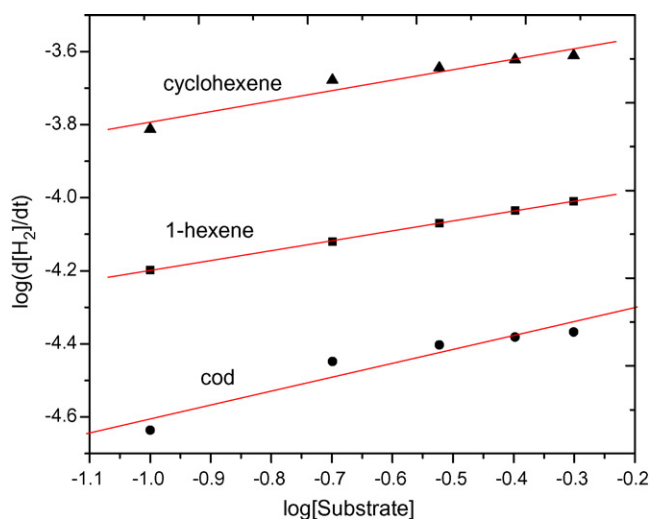**Fig. 6.** Logarithmic plot of initial rate vs. substrate concentration.



**Fig. 8.** Logarithmic plot of initial rate vs. hydrogen concentration.

### 3.2.1. Variation in substrate concentration

The influence of variation of substrate concentration on the rate of hydrogenation was studied over a range of 0.1–0.5 M at a constant catalyst concentration of $14.4 \times 10^{-3}$ M palladium, 1 atm pressure and 303 K. The rate of the reaction showed a linear dependence on the concentration of olefin. The order of the reaction was determined from the slope of the plot of log[initial rate] vs. log[substrate] and was found to be fractional order in all the three cases (Fig. 6). This might be due to the possibility of formation of an intermediate complex involving the substrate [29].

### 3.2.2. Variation in catalyst concentration

The influence of catalyst concentration on the rate of hydrogenation was studied over a range of $2.88 \times 10^{-3}$ to $14.4 \times 10^{-3}$ M palladium at 303K, 1 atm pressure at a fixed substrate concentration of 0.2 M. The rate increased with an increase in catalyst concentration linearly in all cases, indicating the absence of gas liquid mass transfer resistance [30].

The order of the reaction with respect to catalyst concentration was calculated from the slope of the plot of log[initial rate] vs. log[catalyst] and was found to be unity (Fig. 7).
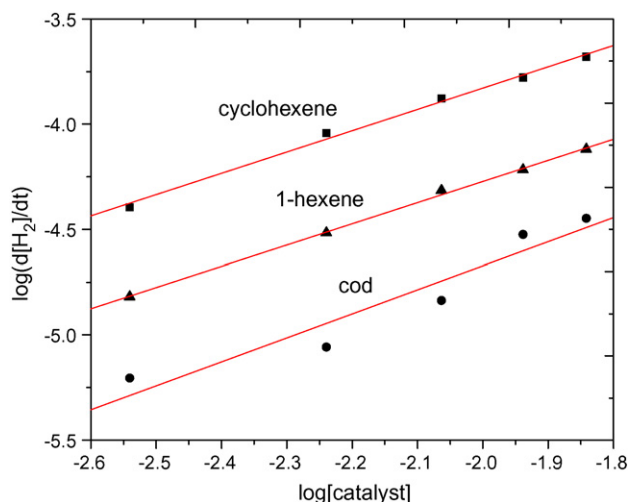
### 3.2.3. Variation in pressure of hydrogen

A range of partial pressure of hydrogen was obtained by mixing pure $N_2$ and $H_2$ in a gas burette so that the total pressure of the mixture of gases was 1 atm. Data on the solubility of $H_2$ in methanol at various partial pressure was calculated using Henry's constant at 303 K [16]. A plot of log[$H_2$] vs. log[initial rate] for various olefins shows a first order dependence (Fig. 8).

Based on the results obtained and evidence from the literature [27], a plausible mechanism is proposed for the hydrogenation of monomers (Scheme 2).

The polymer catalyst in a reversible manner binds to the substrate to form π-complex. In a slow step, the π-complex reacts with hydrogen to form a dihydrido alkyl palladium species which finally undergoes a reductive elimination resulting in an alkane.

A rate law derived for the above mechanism is as follows:
Rate equation

$$\text{Rate} = \frac{Kk_1[\text{catalyst}][\text{olefin}][H_2]}{1 + K[\text{olefin}]}$$

where $K$ is the equilibrium constant for the reversible reaction and $k_1$ is the velocity constant for the rate determining step.

This expression explains the fractional order of the reaction with respect to substrate concentration and first order with catalyst concentration and hydrogen pressure.



**Fig. 7.** Logarithmic plot of initial rate vs. catalyst concentration.
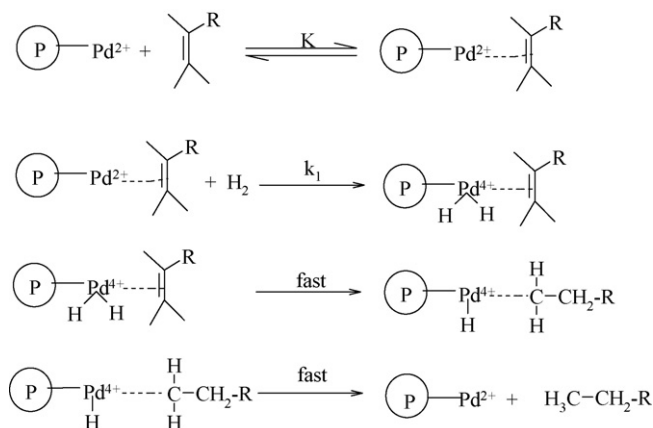


**Scheme 2.** Plausible mechanism for hydrogenation of olefins.

**Table 3**
Hydrogenation of olefins—thermodynamic parameters involving $k_1$ and $K$.

| Substrate | $k_1$ (dm$^3$ s/mol) | $K$ | $-E_a$ (kJ/mol) | $-\Delta H$ (kJ/mol) | $-\Delta G$ (kJ) | $-\Delta S$ (J/K) |
|---|---|---|---|---|---|---|
| 1-Hexene | 2.20 | 17.42 | 25.71 | 23.2 | 7.20 | 247.8 |
| 1,5-Cod | 6.02 | 14.13 | 30.43 | 28.0 | 6.67 | 239.1 |
| Cyclohexene | 1.19 | 8.62 | 45.22 | 42.7 | 5.43 | 174.4 |

From a plot of 1/rate vs. 1/[olefin] at a constant catalyst concentration of $14.4 \times 10^{-3}$ M and 1 atm pressure (Fig. 9), the value of $K$ and $k_1$ for the three substrates is evaluated (Table 3).

### 3.2.4. Arrhenius plot

Energy of activation $E_a$ was obtained from an Arrhenius plot at given catalyst concentration of $14.4 \times 10^{-3}$ M and substrate concentration of 0.2 M (Fig. 10). High value of thermodynamic parameter $\Delta S$ indicates the adherence of the complex on the polymer support. Although $\Delta S$ is negative, the values of $\Delta G$ and $\Delta H$ indicate favourable formation of π-complex in the equilibrium step.
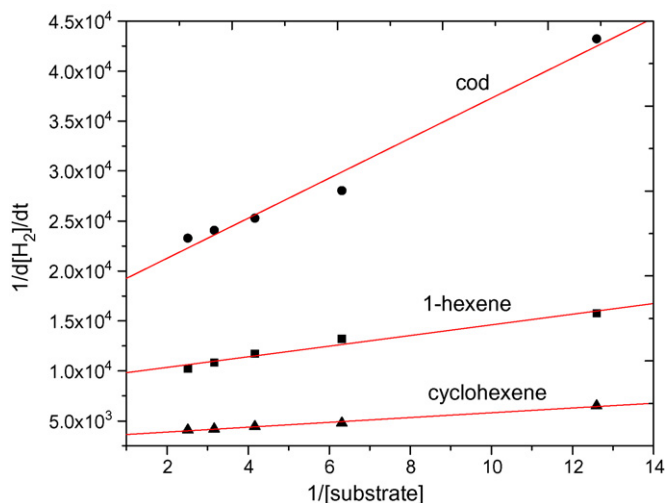


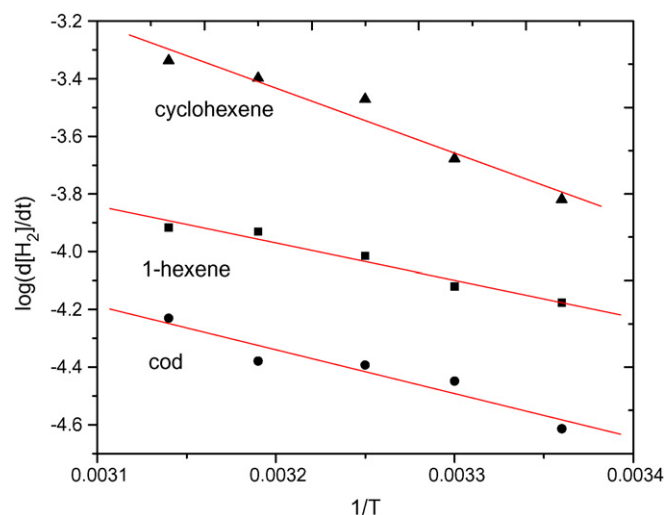**Fig. 9.** Plot of reciprocal of initial rate vs. reciprocal of [substrate].



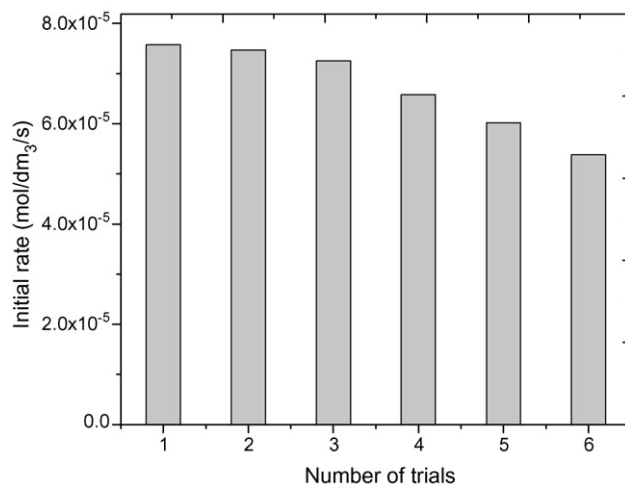**Fig. 10.** Arrhenius plot: log(initial rate) vs. 1/$T$.



**Fig. 11.** Recycling efficiency of catalyst for hydrogenation of 1-hexene at 303 K in 30 ml methanol at 1 atm. H$_2$ pressure, [catalyst] = $14.4080 \times 10^{-3}$ M and [1-hexene] = 0.2 M.

## 4. Recycle of the catalyst

In order to test the stability of the polymer-bound catalyst and to find the recycling efficiency of the catalyst, a known quantity of 1-hexene was reduced and its initial rate was determined. The beads were then filtered, washed, dried and reused. The catalyst was analyzed for its metal content by AAS after the first cycle. No leaching of the metal was observed. Aliquots of the reaction mixture were also analyzed for the metal content at regular interval (every 10 min). Results showed that there was no metal in solution, suggesting that there is no leaching and readsorbtion of metal during the reaction. The results tabulated show a marginal decrease in the initial rate after 3 cycles (Fig. 11). The decrease in the rate may be due to microstructural changes in the catalyst.

The neat complex PdCl$_2$(NSBA) was tested for its catalytic activity in homogeneous conditions. As soon as the methanolic solution of the complex was saturated with hydrogen gas, metal precipitated out of the solution making it unsuitable for the reaction. On the other hand the polymer-supported catalyst did not show any leaching even after 6 cycles and could be recycled over three times without significant change in the reaction rate.

## 5. Conclusion

A palladium Schiff base complex was prepared and tested for its catalytic activity towards hydrogenation of olefin. The homogeneous complex under the reaction conditions was not stable and resulted in metal separation. An economical, reusable heterogenized version of the Schiff base complex was prepared from chloromethylated poly(styrene-divinylbenzene). The Schiff base polymer-bound palladium catalyst was found to be effective in hydrogenation of various olefins and could be recycled several times without significant loss in its activity.

## Acknowledgements

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